THE ADDITION OF GRIGNARD REAGENTS TO THE DIBIPHENYLENEPOLYENES

BY

HORACE ALBERT DEWALD

B.S., Allegheny College, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

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THE ADDITION OF GRIGNARD REAGENTS TO THE DIBIPHENYLENEPOLYENES

Introduction

It has been observed that as the carbon-carbon double bond is activated by increased adjacent unsaturation, it will become more susceptible to attack by organometallic reagents (1). Recently, the first example of the addition of a Grignard reagent to an olefin was found when the multiply-conjugated olefin, dibiphenyleneethylene, was treated with very reactive reagents, such as benzylmagnesium chloride and *t*-butylmagnesium chloride (2). The product of the reaction was the corresponding 1-alkyl-1,2-dibiphenyleneethane.

In the present work, a study was made of the behavior of two vinylogs of dibiphenyleneethylene, 1,4-dibiphenylene-1,3-butadiene and 1,6-dibiphenylene-1,3,5-hexatriene, toward the Grignard reagent.

Discussion of Results

The reactive Grignard reagents, *t*-butylmagnesium chloride, benzylmagnesium chloride, and *p*-chlorobenzylmagnesium chloride, were found to condense additively with 1,4-dibiphenylene-1,3-butadiene under normal Grignard reaction conditions. The products were the corresponding 1-alkyl-1,4-dibiphenylene-2-butenes. Of these reagents, *t*-butylmagnesium chloride was the most effective. After several hours reaction time with this reagent, the diene was converted in better than 90% yield to 1-*t*-butyl-1,4-dibiphenylene-2-butene.

The structures of these products were established according to the procedure of Fuson and Porter (2). For example, the addition complex from the reaction of *t*-butylmagnesium chloride and dibiphenylenebutadiene was treated with benzyl chloride to give 1-*t*-butyl-4-benzyl-1,4-dibiphenylene-2-butene (I). The same compound (I) was obtained

when benzylmagnesium chloride was added to the diene and the complex was allowed to react with *t*-butyl chloride. This could mean only that the alkyl groups were attached to the ends of the original diene system. Furthermore, ozonization of (I) gave one of the expected acids, 9-*t*-butyl-9-fluorenecarboxylic acid. This acid was synthesized by the carbonation of the Grignard reagent from 9-chloro-9-*t*-butylfluorene.

The addition of a Grignard reagent to an olefin should result in the formation of a new carbon-magnesium bond or a new, more complex Grignard reagent. The intermediate adducts that were formed by the condensation of Grignard reagents with the diene behaved as typical Grignard reagents themselves. The addition of water or an alkyl halide to the reaction mixture gave the expected hydrocarbons. Carbonation or acylation of the adduct from *t*-butylmagnesium chloride and dibiphenylenebutadiene gave the corresponding acid and ketone, respectively.

Phenethylmagnesium bromide, *s*-butylmagnesium bromide, and phenylmagnesium bromide failed to add to dibiphenylenebutadiene.

1,6-Dibiphenylene-1,3,5-hexatriene was found to be vulnerable to attack by benzyl- and *t*-butylmagnesium chloride. The product of the reaction was that which would be expected by the attachment of the two potential fragments of the Grignard reagent at the ends of the conjugated triene system in a 1,6-manner. Alkylation or hydrolysis of the reaction mixture then yielded a 1,6-dialkyl-1,6-dibiphenylene-2,4-hexadiene and 1-alkyl-1,6-dibiphenylene-2,4-hexadiene, respectively. These structures were indicated by analogy to the reaction of the same Grignard reagents with dibiphenyleneethylene and di-

biphenylenebutadiene, and by comparison of the properties of the adducts. Oxidative degradation of 1,6-di-*t*-butyl-1,6-dibiphenylene-2,4-hexadiene by ozone gave 9-*t*-butyl-9-fluorenecarboxylic acid.

A novel example of radical interchange (3) for Grignard

reagents and alkyl halides was discovered when dibiphenylenebutadiene was allowed to react with a Grignard reagent (*s*-butylmagnesium bromide or phenylmagnesium bromide) in the presence of *t*-butyl chloride. A product of the reaction was 1,4-di-*t*-butyl-1,4-dibiphenylene-2-butene.

A new type of degradation by ozonization has been observed wherein the final product of the reaction is a new hydrocarbon with one or two less vinylene groups. When the "ozonides" of 1,4-dibenzyl-1,4-dibiphenylene-2-butene and 1,6-dibenzyl-1,6-dibiphenylene-2,4-hexadiene were treated with a mixture of glacial acetic acid and hydrogen peroxide, the product of each reaction was 1,2-dibenzyl-1,2-dibiphenyleneethane. 1-Benzyl-1,2-dibiphenyleneethane was formed when 1-benzyl-1,4-dibiphenylene-2-butene was treated under the same conditions.

In contrast to the addition of Grignard reagents in a 1,4-manner to dibiphenylenebutadiene, phenyllithium was found to add twice in a 1,2-manner to this diene. The products of the reaction were the *meso* and *dl*-forms of *sym*-diphenyldifluorenylethane (4).

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VITA

The author was born on October 25, 1922, in Emlenton, Pennsylvania, where he received his elementary and high school education. In September, 1940, he entered Allegheny College and received the degree of Bachelor of Science from that institution in May, 1944. He was employed by Eastman Kodak Company, Rochester, New York, from June, 1944, to August, 1946. At this time he was inducted into the Army of the United States. Upon discharge from the Army, he entered the Graduate College of the University of Illinois in the fall of 1947. From September, 1949, until June, 1950, he held the Eastman Kodak Company Fellowship.

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